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Dynamic Mechanical Analysis for Glass Transitions in Long Shelf-Life Bread

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———————— ABSTRACT ————————

Dynamic Mechanical Analysis (DMA) showed three thermal transitions in meal, ready-to-eat (MRE) bread, resulting in various degrees of change in the viscoelastic property. The moisture-dependent transition at an extremely low temperature ($-90°C$ to $-50°C$) was due to humectants added, while that at a higher temperature T1 was possibly due to ice melting and the polymer components. T1 increased from $\approx -10°C$ at 29% moisture to $\approx 150°C$ as moisture decreased to 2%. This correlated with hardening of the sample. A moisture independent transition at $\approx 10–15°C$ by DMA was identified as a melting process of lipids (shortening). During storage, the magnitude of tan δ peak decreased but its peak temperature did not change. No evidence of any network could be observed by DMA throughout 3 yr storage.

Key Words: dynamic mechanical analysis, glass transition, storage, bread

INTRODUCTION

SHELF-STABLE "meal, ready-to-eat" (MRE) bread is preserved by controlling water activity a_w, pH, oxygen content, and initial microbial load (Hallberg et al., 1990; Powers and Berkowitz, 1990). Although the bread is microbiologically safe, physical and chemical changes may occur during a shelf-life of up to 3 yr. Normally starchy products are prone to staling which involves a considerable deterioration of flavor, texture and color characteristics in fresh bread.

Bread staling has been thought to be a result of amylopectin crystallization (Kulp and Ponte, 1981; Maga, 1975; Krog et al, 1989). However, it has been postulated that starch crystallization and bread firming were not synonymous (Dragsdorf and Varriano-Marston, 1980). Other factors could be responsible for firming of bread such as moisture migration and gluten functionality change (Willhoft, 1973; Pisesookbunterng and D'Appolonia, 1983; Leung, 1981; Levine and Slade, 1991; Kim-Shin et al, 1991).

Bread staling has been discussed as closely related to changes in the molecular motion of polymer chains, mostly characterized by the glass transition temperature, (Tg) (Levine and Slade, 1991). As described in published references (Levine and Slade, 1988; Zeleznak and Hoseney, 1987; Roos and Karel, 1990; Morris, 1990), Tg is a temperature at which an amorphous molecule changes from a highly immobilized, brittle (glassy) state to a relatively mobile, rubbery state. The Tg responsible for mechanical firmness of bread, namely the "effective" network Tg (Levine and Slade, 1991), has been described to be changing during staling resulting in texture firming of bread. Freshly baked bread has been proposed to give the effective Tg at sub-zero temperature which tends to increase to well above room temperature during staling, reaching 60°C in a completely staled bread indicating network maturation in aging bread (Levine and Slade, 1991).

With water as a plasticizer, Tg of bread polymers has been reported to decrease from about 160°C to near room temperature ($\approx 23°C$) upon increasing of moisture content from ≈ 0

to 20% (Zeleznak and Hoseney, 1987; Hoseney et al, 1986). Because most bread staling experiments involve some degree of moisture loss from the crumb, the increase in Tg during staling mentioned above could be partly influenced by the decreasing moisture content. MRE bread allows us to study bread staling for up to 3 yrs storage with no moisture loss from its hermetically sealed pouch. The "effective" Tg can thus be measured and any maturation of the network can be observed with no artifact of moisture loss. Therefore, our objective was to apply Dynamic Mechanical Analysis (DMA) to determine glass transitions in MRE bread and to identify the "effective" Tg as a function of moisture content and storage time.

DMA theory

The theory of DMA analysis can be found in several published works (Hiemenz, 1984; Billmeyer, 1984; Wunderlich, 1990). DMA applies stress in a sinosoidal wave function as the sample temperature is increasing. The responding strain frequency is either in phase with the stress (if the material is an ideal elastic) or out of phase (if the material is viscoelastic). The "out of phase" may be due to differences of inter- and intra-molecular vibrations that are functions of many factors, one being the space between molecules (free volume). Stress and strain are out of phase by a sinusoidal angle of delta (δ); the loss tangent, tan δ, can be calculated as the ratio between E″ (loss modulus) and E′ (storage modulus). The use of DMA to characterize other foods has been demonstrated (Matthiesen and Iban, 1991).

MATERIALS & METHODS

Materials

We used a standard white bread (SWB) and a long shelf life (MRE) bread. The MRE breads are a straight dough product that are hermetically sealed in a trilaminate polyethylene-aluminum foil-polyester pouch with controlled atmosphere and moisture ($< 1.6\%$ O_2 and < 0.89 a_w at 25°C). The standard white bread was made fresh in our lab via a straight dough method (Nussinovitch et al, 1991). The long shelf-life bread is a specialty military ration which accompanies the MRE Ration and was supplied fresh (Sterling Foods, Inc. San Antonio, TX). The procedure is detailed in Military Specifications (Anon, 1989). The formula for SWB included 57.47% flour, 34.48% water, 3.02% shortening, 2.73% sugar, 0.86% salt, 0.29% calcium propionate, 0.11% potassium sorbate, and 0.11% active dry yeast. The formula for MRE bread included 50.28% flour, 28.96% water, 8.50% shortening, 6.34% glycerol, 2.25% yeast, 1.29% salt, 1.00% sucrose ester, 0.50% gum arabic, 0.50% xanthum gum, 0.25% calcium sulfate, 0.10% sorbic acid, and 0.03% cream flavor.

Methods

The DMA experiment was divided into three parts; SWB and MRE bread comparison, the effect of moisture on thermal transitions, and the storage time study. Various moisture contents were obtained by hydration from original moisture. The hydrated samples were prepared by placing the compressed and cut bread bar described below in desiccators above pure water for 1, 2 and 15 hr. The desorbed samples were prepared by dehydrating in a vacuum oven at room temperature and 30 in. Hg vacuum for 15 min, 2 hr or 24 hr. Final moisture contents were 28.8%, 24.5%, 22.6%, 17.0%, 13.4%, 8.5% and 2.6%

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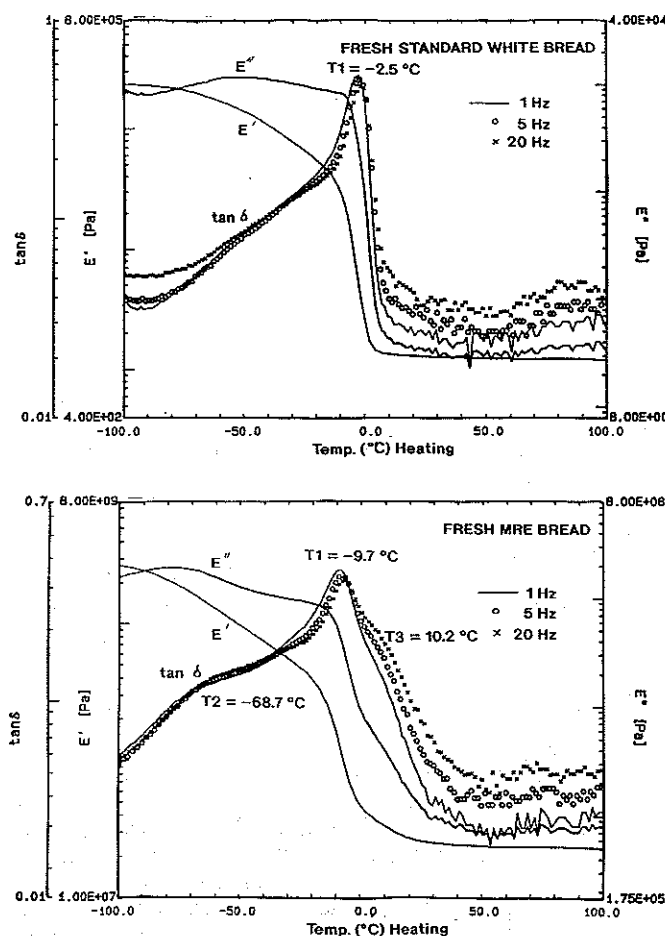
Fig. 1—DMA Thermograms of fresh standard white and MRE breads. The changes in the stored (E') and loss (E") modulus, and the tangent of the loss angle (tan δ) are shown as the samples were heated from −100°C to 200°C at 2°C/min. Solid lines correspond to measurements at 1 Hz frequency. Tan δ at 1, 5, and 20 Hz is represented by 0, and x, respectively.

total weight basis. The storage times for the MRE breads at 22°C were 3 mo, 11 mo, and 3 yr.

DMA Analysis

All samples were uniformly sliced to a thickness of 10 mm, the crust removed, and then the crumb compressed to 2 mm thickness using a Carver press with 21 kg/cm^2 pressure. This pressure was optimum to obtain a uniform thickness of 2 mm with no porous structure remaining. Experiments showed that less pressure resulted in a nonuniform, porous slab that led to a scattered DMA thermogram with much higher experimental error (>15%). The resulting pressed bread was cut with a die into a 50 mm × 12 mm rectangle. Uniform geometry of the sample was critical to prevent variation in the resulting strain. The resulting bars were of 0.10 ± 0.001 g/cm^3 density.

The bread bars were placed in the DMA (Seiko Instruments International, Model DMS110, Terrance, CA). The clamps were left untightened during freezing by liquid N$_2$. When the sample reached −60°C the clamps were tightened and the cooling was continued to −90°C. The strain at that point was tested to be below 10 μm flexure. The sample was then heated from −80°C to +200°C at a rate of 2°C/min. A three point bending head was used and the stress was applied at 1, 2, 5, 10, 20 Hz frequencies. The technique was very sensitive to the sample physical dimension and thus great care had to be given to the sample preparation step to obtain reproducible results. The Tg values varied ± 2.4% experimental error.

RESULTS

Comparison of formula

The tan δ, E' and E" of a fresh standard and MRE breads were plotted vs. temperature (Fig. 1). The resulting E' and E"

started from relatively high values and sharply dropped at ≈ −2.5°C, and −11.0°C for the white and MRE breads, respectively. At those the same temperatures, the tan δ values (ratio between E" and E') rose to a peak and then sharply dropped. This could be either due to a first order transition (melt) or a second order (glass transition, Hiemenz, 1984). To the left of the main transition (T1), there appears to be another small and broad transition at ≈ −70°C, indicated by a shoulder in tan δ accompanied by a slight drop in E'. This T2 transition seemed to be quite noticeable in the MRE bread (T2, Fig. 1b) and almost undetectable in the white bread (Fig. 1a). In addition, the MRE bread showed another strong shoulder in tan δ to the right of the main transition peak (T3, Fig. 1b) where the white bread did not (Fig. 1a).

The sharp single tan δ peak in the white bread at −2.5°C (Fig. 1a) indicated that there was one transition. On the other hand, presence of shoulders of tan δ found in the MRE bread, indicated there were 2 additional transitions detectable under those conditions. Tan δ at various frequencies illustrated (Fig. 1), showed the temperature shifted to a higher value at a higher frequency. The main thermal transitions (T1) in white bread (−2.5°C) and MRE bread (−9.7°C) occurred simultaneously with ice melting. DSC (Differential Scanning Calorimetry, 10°C/min) scans of the samples (Fig. 2) showed a corresponding endothermic melting of ice. The endotherm To (initial temperature) occurred at −10.1±0.4°C for SWB and at −18.3±0.2°C for MRE bread. In addition to melting of ice, there was a shift in the DSC baseline after the ice melting process was completed. This resulted in a relatively lower baseline to the right of the endothermic curve (Fig. 2). This was reasonable since ice and liquid water are different in specific heat and thus melting of ice would result in an increased heat capacity in the sample, resulting in lowering of the baseline. Note also there was a possibility that, once melted, the frozen water became liquid and able to plasticize bread polymers. Thus an instantaneous plasticization and a glass transition of the polymers is also possible. This would result in an additional change in heat capacity. How significant this process may be in changing the sample heat capacity is yet to be determined.

Also indicated (Fig. 2) is a DSC result at −110°C to −26°C range showing a baseline shift (more evident with 5°C/min scan, see Fig. 2), indicating a glass transition process. Thus, the T2 transition (Fig. 1b) was confirmed to be a glass transition. This was due to the presence of glycerol in MRE bread. This glass transition was not found in SWB because of the lack of glycerol.

Comparison of moisture content

The effects of moisture on DMA thermograms were investigated. Tan δ was most sensitive to the moisture variation in the samples. For clarity of the presentation, only tan δ is illustrated in Fig. 3. In addition, E' and E" absolute values are known to vary among samples since they were most sensitive even to small variations in geometry and density. Fresh MRE bread adjusted to various contents (2.6–28.8% wet basis) showed significant changes in DMA thermograms as indicated by the shift in tan δ peaks (Fig. 3). As the moisture content decreased from 28.8%, the main transition (T1) became less predominant. At 17.0% moisture, only one relatively broad transition remained. As moisture content continued to decrease, the peak temperature increased. The peak temperature of this T1 transition, once plotted vs moisture content, gave the curve T1 (Fig. 4). The T2 transition at ≈ −70°C was only observed at moisture 17.0% and above. Plotting T2 peak temperature against moisture content gave the T2 curve (Fig. 4). And lastly, the T3 transition which seemed to be a small shoulder to the right of T1 in the high moisture sample (Fig. 3) stayed at its range of temperature (8–14°C) regardless of changing moisture. Thus once this was plotted vs moisture content (Fig. 4), this T3
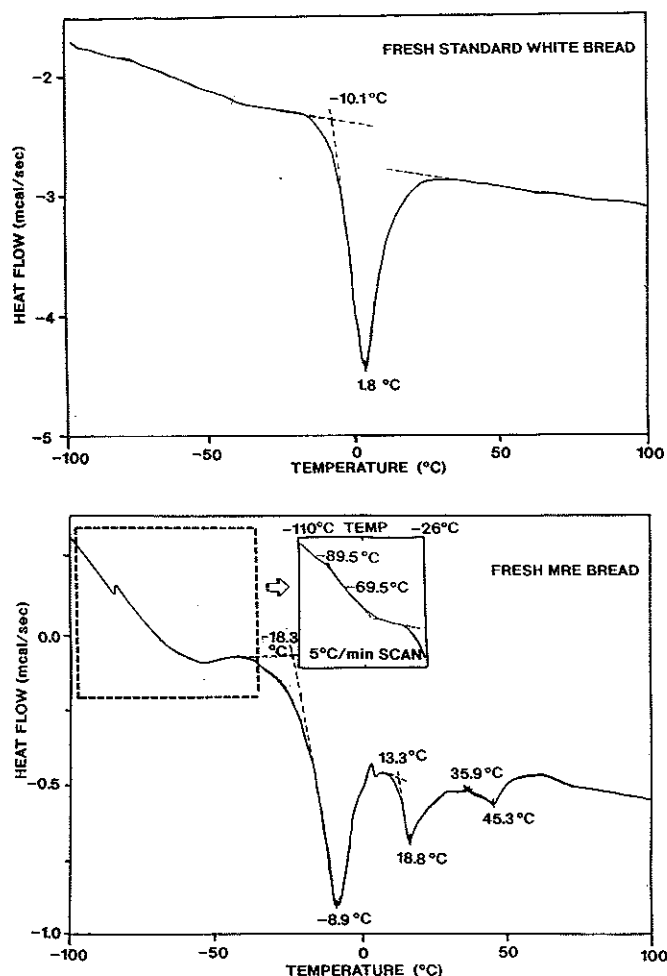
Fig. 2—DSC thermograms of fresh standard white bread and of fresh MRE bread. Samples were heated from −100°C to 100°C at 10°C/min in hermetically sealed pan.

Fig. 3—DMA thermogram for tan σ values in fresh MRE breads adjusted to various moisture contents (2.6–28.8%; wet basis). The identified peaks of tan δ, T1, T2 and T3, corresponded with a decrease in E' and E". All curves presented on the same γ axis scale (tan δ upto 1.0 value scale) and are overlaid here for clarity.

Fig. 4—Thermal transition temperatures of fresh MRE bread as a function of moisture content.

curve remained constant over the entire moisture content. Note that T3 is not ice melting since its peak temperature was above melting point of ice. Also note that characterizing of the tan δ peak (Fig. 3) might appear difficult. Once all observed peak temperatures were plotted (Fig. 4), it became evident and matching the transition (T1, T2, T3) with the tan δ peaks became easier. It is clear from Fig. 4 that there were three distinct transitions in a fresh MRE bread, 2 moisture dependent transitions (T1 and T2) and one moisture independent transition (T3).

The T1 transition was most affected by moisture particularly at the range between 2% and 20% (Fig. 4). The transition temperature was found to decrease from ≈160°C at 2.6% moisture to −11.0°C at 28.8% moisture. This temperature was within the range of Tg for gluten and starch reported by others (Hoseney et al., 1986; Levine and Slade, 1991; Morris, 1990). The second transition (T2, Fig. 4) a glass transition (see DSC results above) occurred at very low temperatures, ranging from −60°C to −90°C. Having such a low Tg temperature, this moisture dependent transition was most likely a result of water-soluble solutes. This may be due to the presence of 6.34% glycerol (total dough weight basis) in the MRE bread. Glycerol has been reported to show a glass transition temperature of −65°C (Levine and Slade, 1988). The DSC data (Fig. 2b) also gave the average Tg of −69.5±1.3°C in fresh MRE bread. White bread contained no glycerol and thus gave no T2 transition.

The moisture independency of the third transition (T3, Fig. 3) indicated that T3 was due to water-immiscible components.
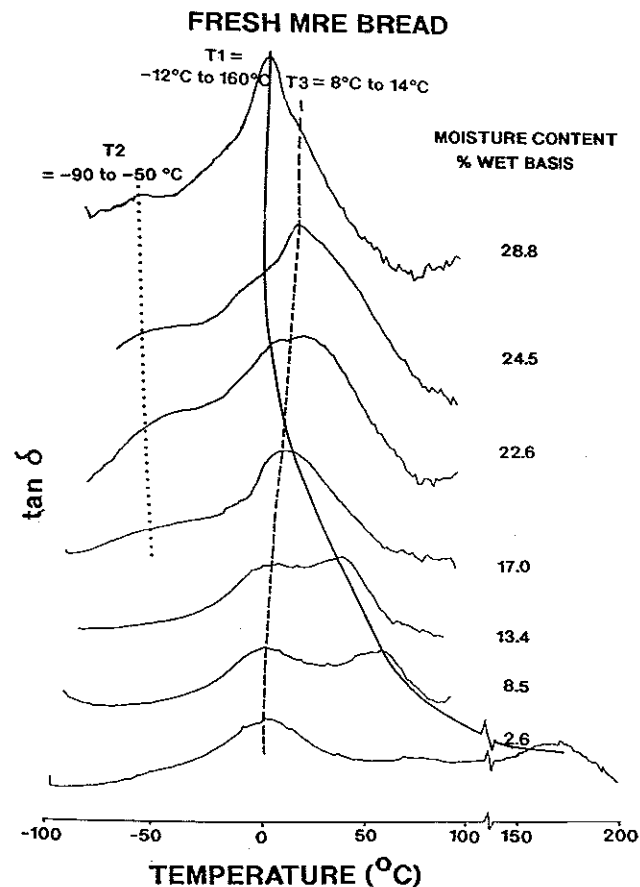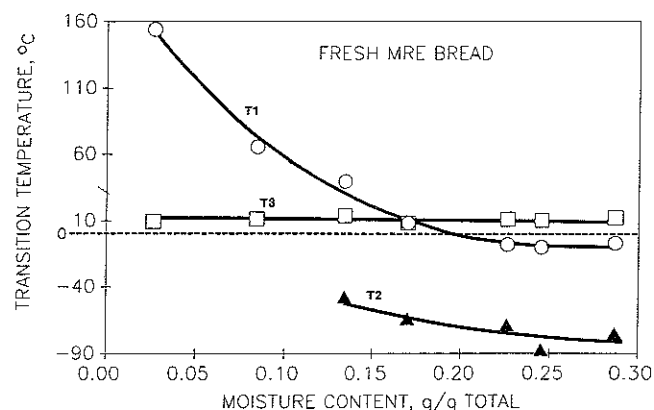
These could include shortening and hydrophobic domains of bread components. The absence of T3 transition in the fresh standard white bread (Fig. 1a) was partly due to the relatively small amount of shortening added. The DSC (Fig. 2b) confirmed that there were two endothermic melting processes at temperatures above zero. One of these fell in the temperature range corresponding to T3 indicated by the DMA results (Fig. 1b).

Comparison of different ages

MRE bread samples stored at room temperature up to 3 yr yielded thermograms as illustrated (Fig. 5). The fresh sample
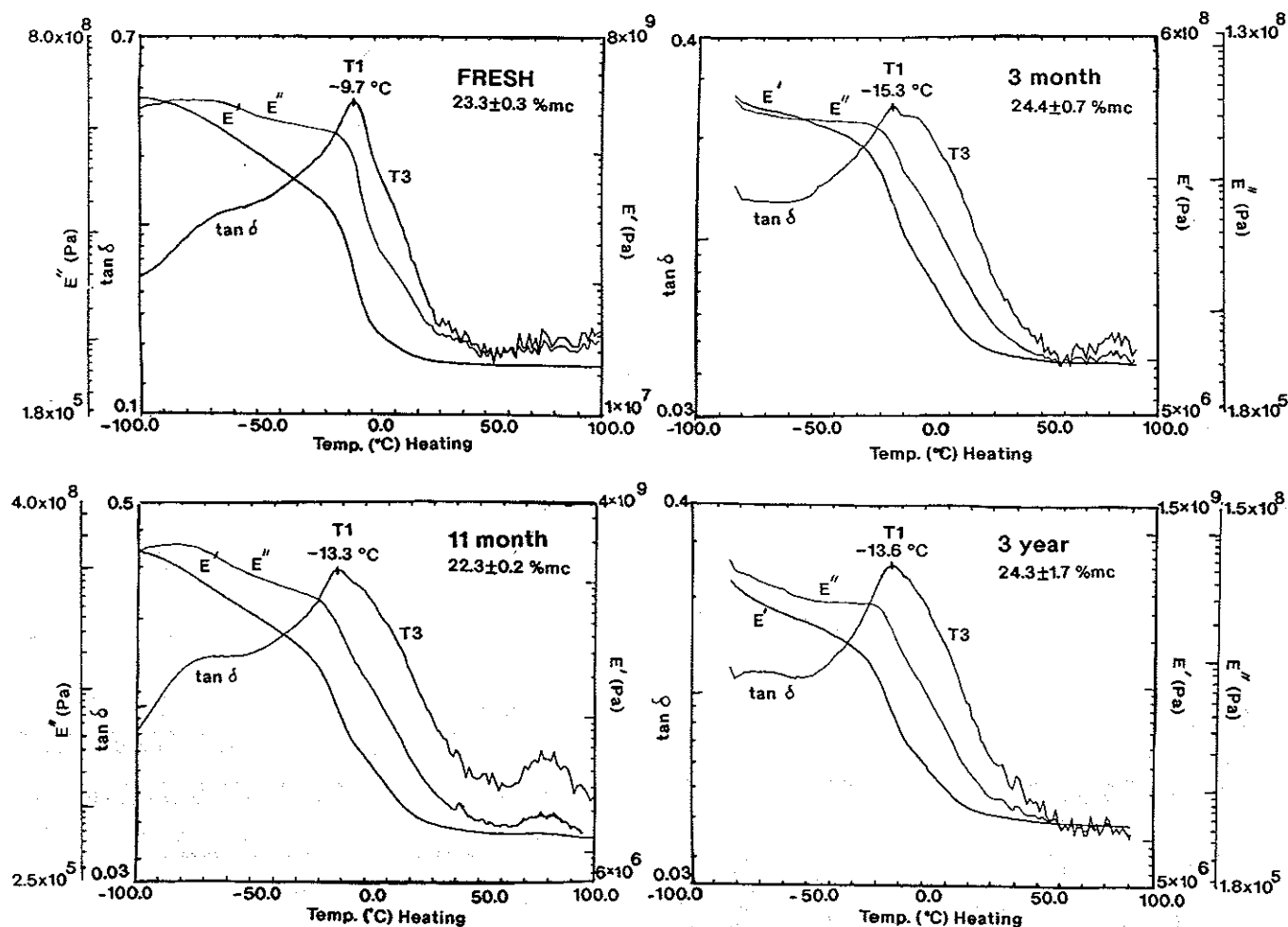
Fig. 5—DMA thermograms of MRE breads stored in hermetically sealed pouches at room temperature for various periods up to 3 yr.

showed a sharp T1 transition at a tan δ peak temperature of −9.7°C, with a very small right shoulder. As the bread aged for 3 mo, the T1 transition became much less prominent (from 0.45 tan δ for fresh bread to 0.25 tan δ for 3 mo old bread), and thus the right shoulder (T3) became more observable. However, there were no significant changes in either T1 or T3 temperatures with storage time.

In the 3 mo and 11 mo old samples (Fig. 5), some DMA data showed that could be identified as a small peak in tan δ at 60–90°C temperature range. However, the E' and E" values did not change considerably. This might be evidence of some slight melting process of retrograded starch. No such evidence was found in the 3 yr sample, however.

According to Levine and Slade (1991), a maturation process of polymer network during bread staling leads to another glass transition ("effective Tg") at some higher temperature (max 60°C). Our data (Fig. 4) indicated no development of such "effective Tg" transition over time. In addition sample firmness as measured by the stress-strain curve (Instron data, not shown) increased only slightly during the first 3 mo and then leveled off for the rest of the storage period. Over the 3 yr period, the sample remained relatively soft and acceptable, unlike a staled bread. This confirmed the fact that there was no evidence of a mature network formation in MRE bread during storage.

CONCLUSION

DMA has been found sensitive to phase transitions detected by a combination of a decrease in E' and E" a peak in tan δ as the bread sample approached the transition temperature. The

transition found in fresh white bread was identified as ice melting that occurred simultaneously with a change in heat capacity. In MRE bread, presence of small water-soluble solutes was suggested to be responsible for the low temperature Tg transition (−70°C range). Biopolymers (e.g. starch, gluten and gums) gave the higher temperature transition T1 (−9.7°C), which was found to occur simultaneously with ice melting. As moisture content decreased, T1 increased reaching a value of 160°C at 2% moisture. MRE bread storage study revealed that the transition temperatures remained relatively unchanged throughout the 3 yr storage, indicating no evidence of any mature network. This was probably because the bread did not lose moisture during storage and thus the effective Tg did not change. A small, noisy tan δ peak at 50°C in some samples stored for 3 and 11 mo (not for 3 yr), may be evidence of retrograded starch.

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